PERFORMANCE OF PLASTIC PACKAGING FOR HAZARDOUS MATERIALS TRANSPORTATION

PART VI MASS LOSS AND EFFECTIVE CARBON ATOM NUMBER MEASUREMENT

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Part VI: Mass Loss and Effective Carbon Atom Number Measurements

by

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Abstract

This report describes the mass loss through polyethylene bottles of two n-alkyl series (n-alcohols and n-carboxylic esters) and a group of miscellaneous compounds. The experiments were performed at 50 °C using both low density and high density polyethylene bottles. The backbone chain length, N_A, for each series of n-alkyl's was extended to 16 in order to characterize more fully the dependence of loss rate from PE on chain length of permeant.

The results suggest that the effective carbon atom number for a given permeant may be determined from a single density resin bottle using the n-alkane series as the standard lading. Once the effective carbon atom number has been determined under chosen conditions, the permeability performance of the permeant for another resin density may be predicted with reasonable accuracy. These results seem to complement the "permachor" method to minimizing the number of tests required for the determination of the performance of full-scale containers.

Preface

This report is part VI of a series prepared for the Office of Hazardous Materials Operations under Research Contract DOT AS-50074. This work deals with the establishment of criteria for predicting permeation performance of various kinds of ladings in polyethylene bottles. This study verifies, at least for the permeants and containers studied herein, the validity of the effective carbon atom number as a parameter for transferring results of permeation measurements among various shipping containers made from various PE resin. The present work extends the concepts presented in Part IV of this series.

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Introduction

The permeation rate of vapors and gases through a given barrier material depends on parameters such as thickness, density of the material, and the compatibility of the permeant and the barrier [1]. Various attempts at correlating permeability with these barrier parameters have proven successful in many instances and have also made possible the prediction of the transmission performance of a given barrier and the permeant [2,3]. In a previous report to DOT (Part IV, DOT AS-50074), an effective carbon atom number was introduced as a parameter for predicting permeation performance of n-alkanes in PE bottles [4]. This present report has attempted to establish the validity of the effective carbon atom number by: (1) studying other homologous series; and (2) looking at a wider range of densities of the PE resin.

This work investigated the loss rate for an n-alcohol series (N_A = 1 to 16) and an n-carboxylic ester series (N_A = 5 to 16) in PE bottles of two different densities (ρ~ .92 g/cm and ρ~ .94 cm) at 50 °C. The effective carbon atom number was determined for each permeant and found to be relatively insensitive to the density of both PE resin bottles [4]. By using the average effective carbon atom number, the loss rate in the high density PE bottle was predicted for a group of miscellaneous compounds (1,2-dichloroethane; acetone; methyl ethyl ketone; acetonitrile) from the loss rate measurements in the low density PE bottle with rather good agreement to the experimental data. These results tend to support the statistical linear model for transmission rate as outlined in part IV of the permeation report DOT AS-50074.

Materials

A. Ladings

The n-alcohols (N_A = 1 to 16), n-carboxylic esters (N_A = 5 to 16), and a group of miscellaneous compounds used in this study are listed in Table II. All samples were either A.C.S. certified, reagent or technical grade and were used without any further purification.

B. Polyethylene Bottles

Table I lists some information on the PE bottles used in this study. The low density (CPE, $\rho \sim .92$ g/cm) and high density (LPE, $\rho \sim .94$ g/cm) bottles were manufacturered by the Nalge Company. The actual densities, as determined by a flotation method using ethanol and distilled water at 25 °C, were found to be $\rho = .9235$ g/cm^3 and $\rho = .9453$ g/cm^3. Some high density PE bottles made by Phillips Petroleum Company were found to have a density of $\rho = .9430$. The mean wall thickness of the CPE and LPE bottles were, respectively, .1062 cm and .0950 cm and the "Phillips" bottles had a mean thickness of .0671 cm. The CPE bottles as shown in Table I showed the greatest variation in thickness over its wall surfaces while the "Phillips" bottle had the least variation. Such density and thickness fluctuations for a given bottle contributes to the uncertainty in the mass loss measurement.

Experimental

Mass loss measurements were performed in a safety-designed air circulating oven maintained at 50.0 °C ± 0.4 °C. Marked positions within the oven were calibrated for temperature variations and during the experiment, the oven temperature was monitored by a thermistor probe. The zero time of the experiment was taken as the initial placement of the bottles

(filled with ~100 m ℓ of sample) into the oven [4]. At subsequent times, the bottles were removed and weighed on a top-loading balance sensitive to about .01 g. From the change in mass versus time, the loss rate for each sample was determined.

Results and Discussion

A. Mass Loss

Typical curves for mass loss measurements are shown in Figs. 1-8. All the curves seem to posses the same general mass-time behavior, i.e., as the time increases beyond the induction period, the curves tend to asymptotically approach linear behavior. From permeation theory [5] such behavior may be represented as

$$\Delta m = \left[\frac{\partial \Delta m}{\partial t}\right] (t - \underline{q}\ (t/\tau)\tau) \qquad (1)$$

where Δm is the amount of permeant lost after time t, $[\partial \Delta m/\partial t] = \dot{Q}$ is the steady-state rate of loss, $\underline{q}$ is a parameter which depends on the molecular transport process and the initial experimental conditions and τ is the time-lag which is proportional to the thickness of the container wall, ℓ, and inversely proportional to the diffusivity of the permeant, D, i.e., $\tau = \ell^2/6D$.

The mass-time data for this study have been analyzed only in terms of the steady-state rate, $\dot{Q}$, and is summarized in Table II and Figs. 9 and 10. As can be seen in Fig.1, Figs. 3-6, and in Table II, an increase in PE density tends to diminish the amount and rate of permeant passing through the container walls. If the diffusion process is truly Fickian, then the steady-state rate should be inversely proportional to the effective thickness for a constant area [4]. The results in Fig.1 and

Table I and II for the "Phillips" bottle do indeed suggest an inverse dependence of $\dot{Q}$ on ℓ, but a small difference in density (as will be shown later) could also appreciably increase the loss rate.

The results in Table II and Figs. 9 and 10 further suggests a dependence of loss rate on chain length as expected. Here the chain length is defined as the backbone or skeletal chain length, N_A, which includes all atoms in the primary chain [6] exclusive of atoms at the chain end that constitute a chemical group (e.g., CN, NH_2, OH, etc.). The loss rate, $\dot{Q}$, may be empirically defined [3] as:

$$\dot{Q} = \dot{Q}_o e^{-E_p/RT} \qquad (2)$$

where $\dot{Q}_o$ is a constant, E_p is the apparent activation energy, R is the gas constant, and T is the absolute temperature. Since the apparent activation energy generally increases as the chain length increases, the loss rate according to Eq.(2) should decrease. For chain lengths below some critical value, ($N_A \sim 5$) the loss rate may not be a monotonic function due to polarity effects [3] as shown in Figs. 9 and 10 for the n-alcohol and n-carboxylic ester series. Two members of the ketone series (acetone and MEK) also seem to show polarity effects for the early members of the series. The results in Figs. 9 and 10 also suggest that as the chain length increases, the loss rate for each series tend to approach that of the n-alkanes.

B. Effective Carbon Atom Number

The effective carbon atom number, n_e, is just a shift parameter that characterizes the loss rate of a given permeant to that of some standard or reference permeant [4]. This concept is analogous to that

of the "permachor" approach [3]. In order to account for all atoms in the primary chain, the backbone or skeletal chain length, N_A, is used in this study rather than only the number of carbon atoms in the chain. The choice for the former appear to be small and roughly constant.

Figure 9 for low density PE may be used to illustrate the determination of n_e for a given permeant. For example, the effective carbon atom number for n-amyl acetate is found by shifting at constant loss rate to the n-alkane curve (note dotted line in Fig.9). The abscissa at the intersection of the two curves is defined as n_e. Hence, the determination of n_e may be given mathematically as:

$$n_e = \log (\dot{Q}_A/\dot{Q}_o)/k \tag{3}$$

where $\dot{Q}_A$ is the loss rate for a given permeant, $\dot{Q}_o$ and k are parameters that may be determined from the loss rate equation for the n-alkanes, i.e.,

$$\log \dot{Q} = \log \dot{Q}_o + kN_A \tag{4}$$

By using Eqs.(3) and (4), the effective carbon atom number was calculated from the results in Figs. 9 and 10. In Fig.11 a semi-log plot of loss rate and n_e for both PE density bottles does indeed yield parallel lines within experimental error. The average n_e values for both PE density bottles are assembled in Table III with a maximum deviation of about 10% which occurred in the alcohol series. The lines in Fig.11 may be represented as:

$$\log \dot{Q}_A = F(\rho_p,T) + k_o n_e \tag{5}$$

where F is a function of PE density and temperature and k_o is apparently independent of PE polymer density. By using Eq.(5) and loss rate results

for the miscellaneous compounds in Table II for the low density PE bottles, the loss rate for the high density PE bottle was predicted as shown in Table IV. The results are in rather good agreement with the experimental values and tend to reaffirm the validity of the effective carbon atom number [4]. Similar calculations may also be done for the other compounds with comparable agreement. Figure 12 further illustrates the fact that for $N_A > 5$ the nature of the steady-state diffusion process in the PE polymer matrix is somewhat similar for each series of permeants.
If Eq.(5) is now combined with the results of Fig.11, the loss rate of the permeant at constant temperature becomes:

$$\log \dot{Q}_A = F(\rho_p, T) + k_o n_e = \log \dot{Q}_{Ao} + C(\rho_p - \rho_{po}) + k_o n_e \qquad (6)$$

where C is a constant, ρ_{po} and ρ_p are, respectively, the density of PE for the reference or standard state and ρ_p is some other PE density of interest. Thus at constant temperature, the loss rate for a given permeant may be estimated by Eq.(6) from a knowledge of only n_e and $\dot{Q}_{Ao}$. The latter quantity is determined from the n-alkanes in the standard state. As discussed above, the effective carbon atom number of a given permeant may be experimentally determined from some standard permeant in a given polymer resin.

Conclusion

This work has presented data at constant temperature on mass loss and loss rate for n-alcohols and n-carboxylic esters and a group of miscellaneous compounds of two different densities in PE resin bottles. From the data an effective carbon atom number, n_e, for each permeant was determined and found to be roughly independent of the density of the PE polymer matrix. By measuring loss rate of the n-alkanes as standard permeants in PE bottles of a given density, the loss rate of other permeants may be predicted at some other PE density with reasonable accuracy by using n_e values.

This work further suggests that a standard measurement system of bottles (constant wall thickness, density, type, etc.) and permeants (e.g., n-alkanes) could be chosen for obtaining quantitative mass loss information. Effective carbon atom numbers derived from such measurements could be compiled into a common data pool [4] and made accessible to the concerned community (manufacturers, shippers, users, etc.) for the purpose of ascertaining permeation performance. An assemblage of information of this kind could also aid rulemaking efforts in attempting to normalize such diversified community interests [4].

This investigation has not addressed the question of the dependence of loss rate on temperature. Such studies are highly desirable for ascertaining the activation energies as a function of chain length which enters directly into Eq.(2). Another question of equal importance is the dependence of loss rate on container wall thickness, ℓ. Limited results reported here do indicate an inverse dependence on ℓ, but more extensive and well-defined experiments need to be done in order to predict the permeation performance of full-scale containers with some degree of confidence.

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5. Crank, J. and Parks, G. S., Methods of Measurement, Chapter 1 in Diffusion in Polymers, J. Crank and G. S. Park, Eds., (Academic Press, New York, 1968.)

6. Bondi, A., "Physical Properties of Molecular Crystals, Liquids and Glasses", John Wiley & Sons, Inc., New York, NY (1968).

TABLE I

Polyethylene (PE) Bottles Used For Mass Loss Measurements

TYPE	Density, g/cm^3 Stated	Density, g/cm^3 Found	Average Thickness, cm	Volume Capacity, mℓ
CPE (Low Density)[a]	.92	.9235 ± .0009	.1062 ± .0190	125
LPE (High Density)[a]	.94	.9453 ± .0012	.0950 ± .0068	125
"Phillips" (High Density)[b]	-	.9430 ± .0030	.0671 ± .0028	125

[a]Nalge Company

[b]Phillips Petroleum Company

TABLE II

Loss Rate at t = 50 °C for Various Classes of Compounds

Using Low Density (CPE) and High Density (LPE) Bottles.

N_A[a] Alkane	$\dot{Q}_A$ (g/hr) CPE	LPE	N_A[a] n-Carboxylic Esters	$\dot{Q}_A$ (g/hr) CPE	LPE	N_A[a] n-Alcohols	$\dot{Q}_A$ (g/hr) CPE	LPE	N_A[a] Misc. Compounds	$\dot{Q}_A$ (g/hr) CPE	LPE
7 Heptane	.397	.0677	5 Ethyl Acetate	.0696	.0132	1 Methyl	.00390 .00430	.00142	1 Aceto - nitrile	.00750	.00210
"Phillips" bottle		.0837	7 Butyl Acetate	.0669	.0112	2 Ethyl	.00290 .00320	.000910	2 1,2 - dichloro-ethane	.242	.0470
16 Hexadecane	.0254	.00645	8 Amyl Acetate	.0540	.00800	3 Propyl	.00275 .00320	.000810	3 Acetone	.0240	.00450
"Phillips" bottle		.00973	9 Methyl Heptanoate	.0380		4 Butyl	.00380 .00360	.000890	4 MEK	.0450	.00820
			16 Methyl Tetradecanoate	.0135	.00336	6 Hexyl	.00384	.000670			
						8 Octyl	.00301	.000550			
						10 Decyl		.000478			
						12 Dodecyl	.00248	.000395			
						16 Cetyl	.000897	.000150			

[a] N_A is the backbone or skeletal chain length.

TABLE III

Average Effective Carbon Atom Number for Various Classes of Compounds (based on skeletal chain length)

N_A	n-Alcohols	n_e
1	Methyl	21.8
2	Ethyl	23.0
3	Propyl	23.3
4	Butyl	22.7
6	Hexyl	23.4
8	Octyl	24.1
10	Decyl	26.0
12	Dodecyl	25.1
16	Cetyl	28.5

N_A	n-Carboxylic Esters	n_e
5	Ethyl Acetate	12.9
7	Butyl Acetate	13.2
8	Amyl Acetate	14.2
9	Methyl Heptanoate	14.6
16	Methyl Tetradeconoate	15.1

N_A	Miscellaneous Compounds	n_e
1	Acetonitrile	21.1
2	1,2-Dichloroethane	8.4
3	Acetone	19.0
4	Methyl Ethyl Ketone (MEK)	17.0

TABLE IV

Predicted Loss Rate at 50 °C For
High Density Bottle From Loss Rate of
Low Density Bottle (Using Fig.11)

N_A	Miscellaneous Compounds	Loss Rate, $\dot{Q}_A$ (g/hr) [High Density]	
		Actual	Predicted
1	Acetonitrile	.00210	.0013
2	1,2-Dichloroethane	.0470	.041
3	Acetone	.00450	.0041
4	Methyl Ethyl Ketone (MEK)	.00820	.0077

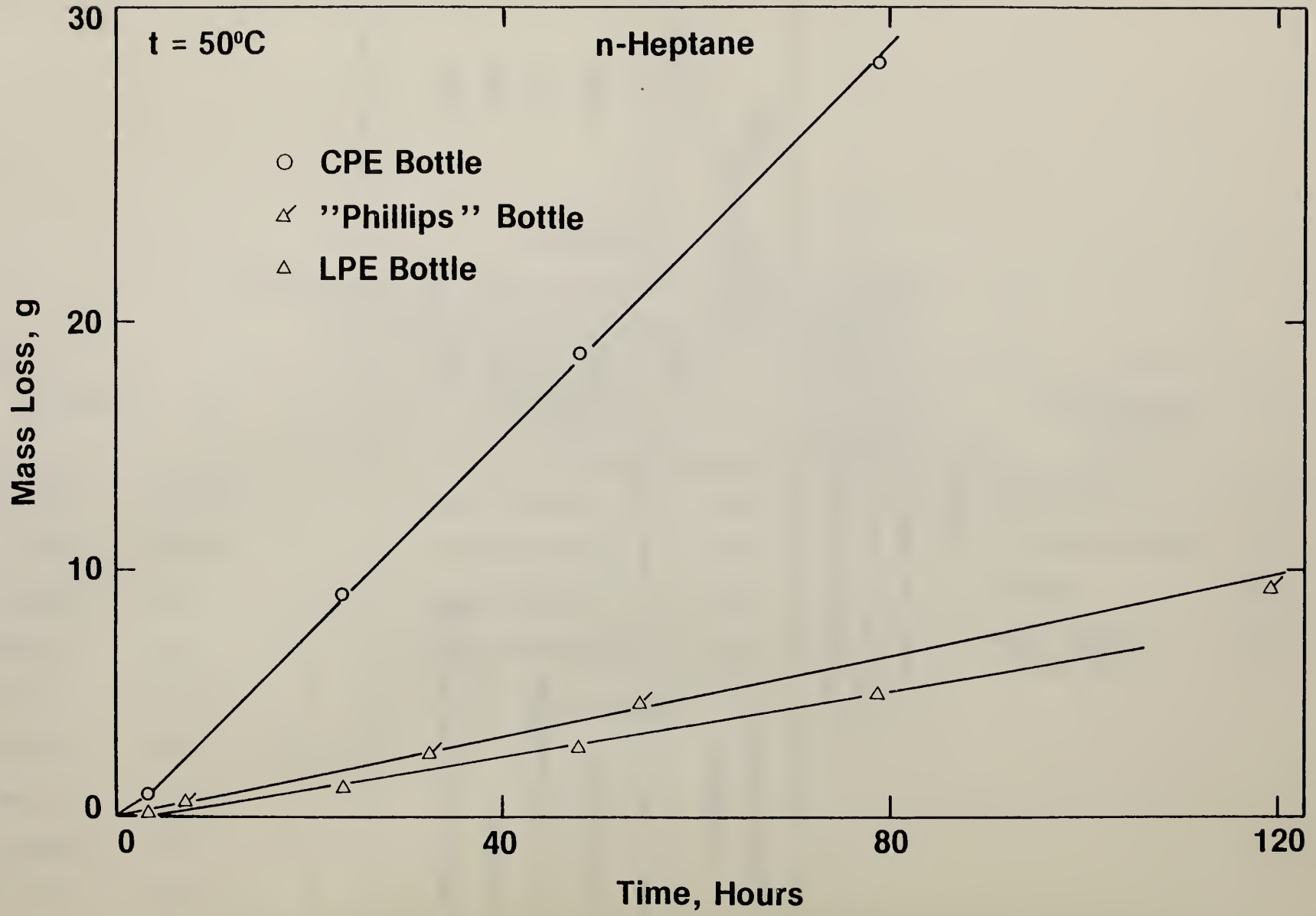
t = 50°C
n-Heptane
CPE Bottle
''Phillips'' Bottle
LPE Bottle
Mass Loss, g
30
20
10
0
0
40
80
120
Time, Hours

Fig. 1

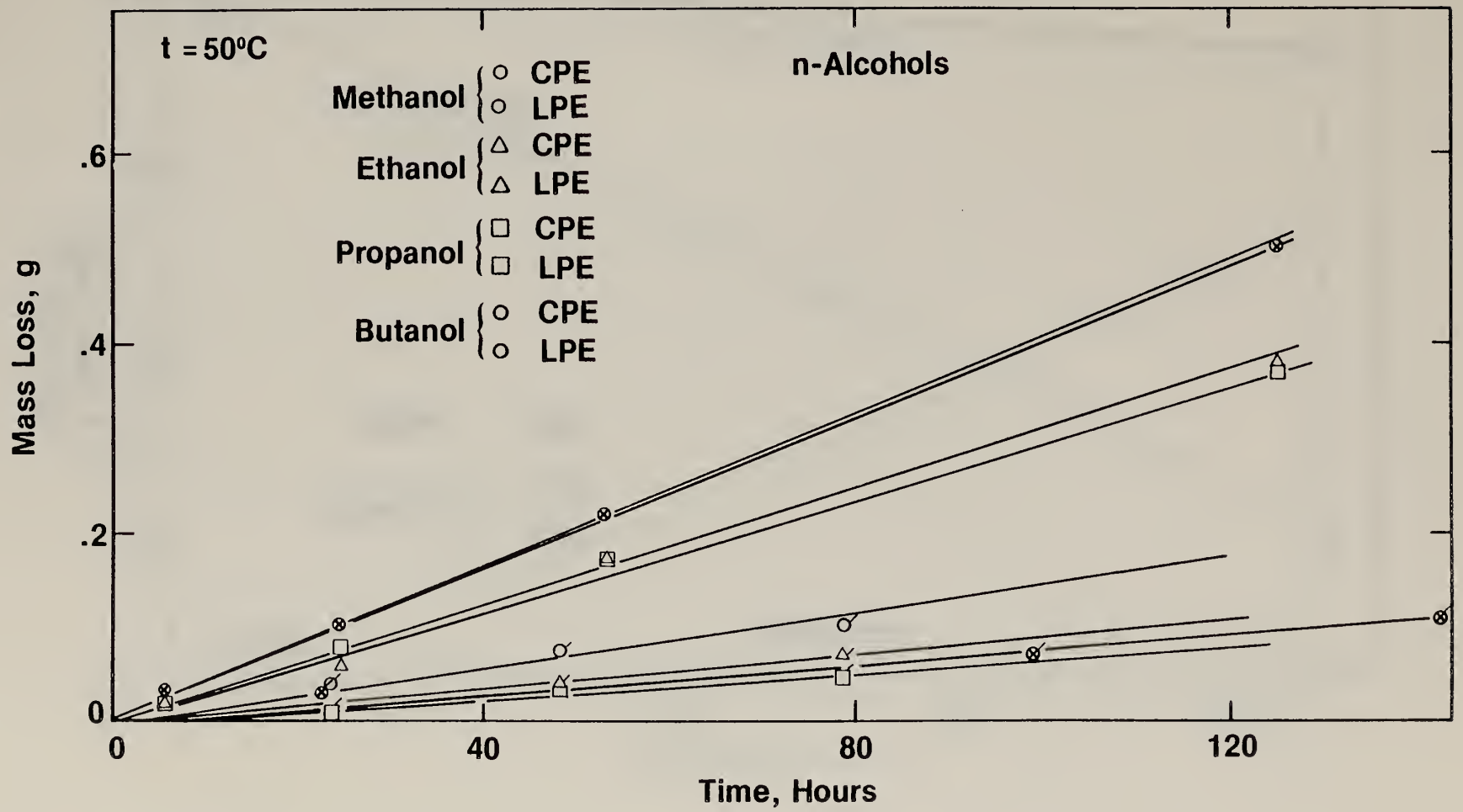
t = 50°C
n-Alcohols
Methanol
CPE
LPE
Ethanol
CPE
LPE
Propanol
CPE
LPE
Butanol
CPE
LPE
Mass Loss, g
0
.2
.4
.6
0
40
80
120
Time, Hours

Fig. 2

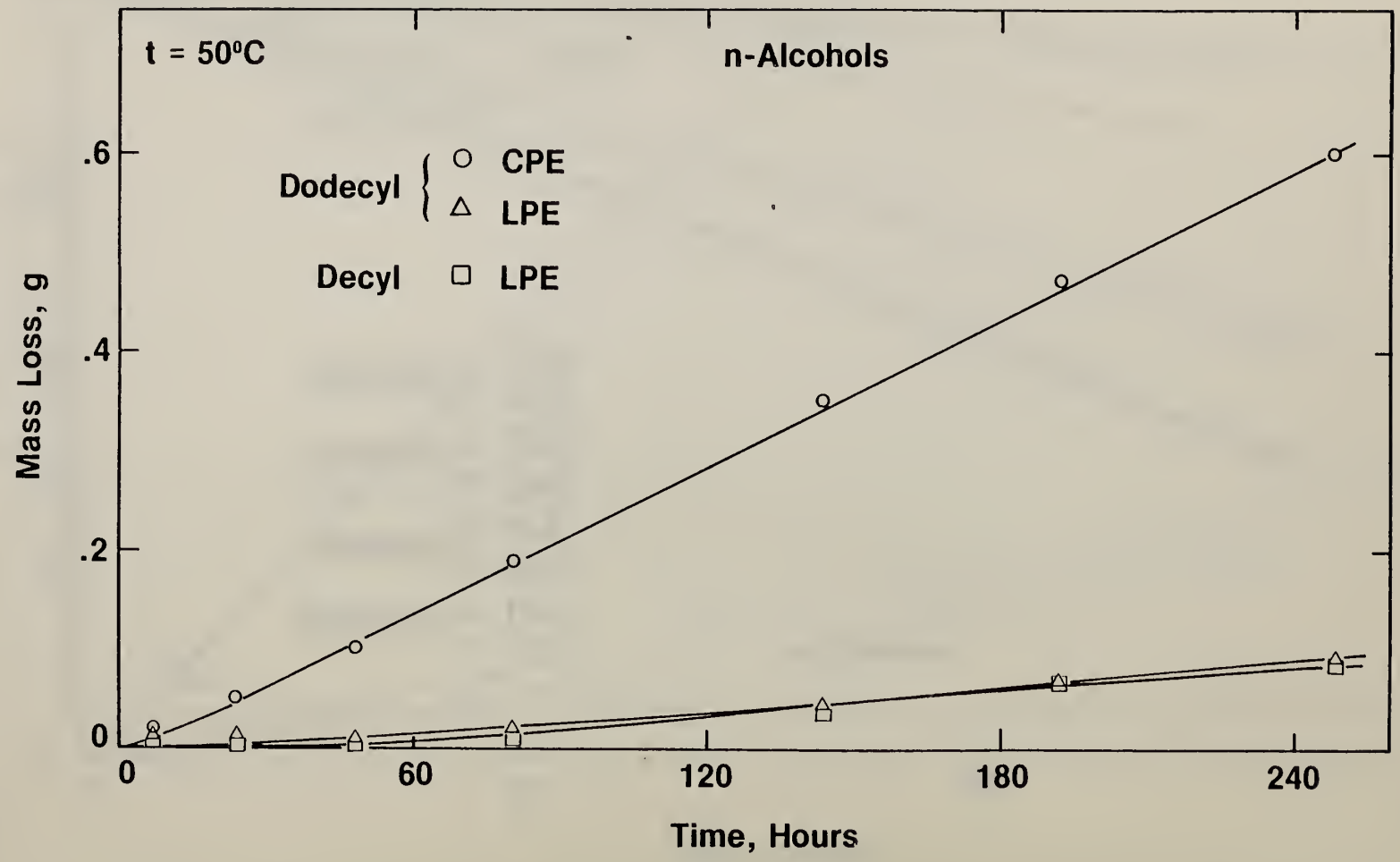
t = 50°C
n-Alcohols
Dodecyl
CPE
LPE
Decyl
LPE
Mass Loss, g
.6
.4
.2
0
0
60
120
180
240
Time, Hours

Fig. 3

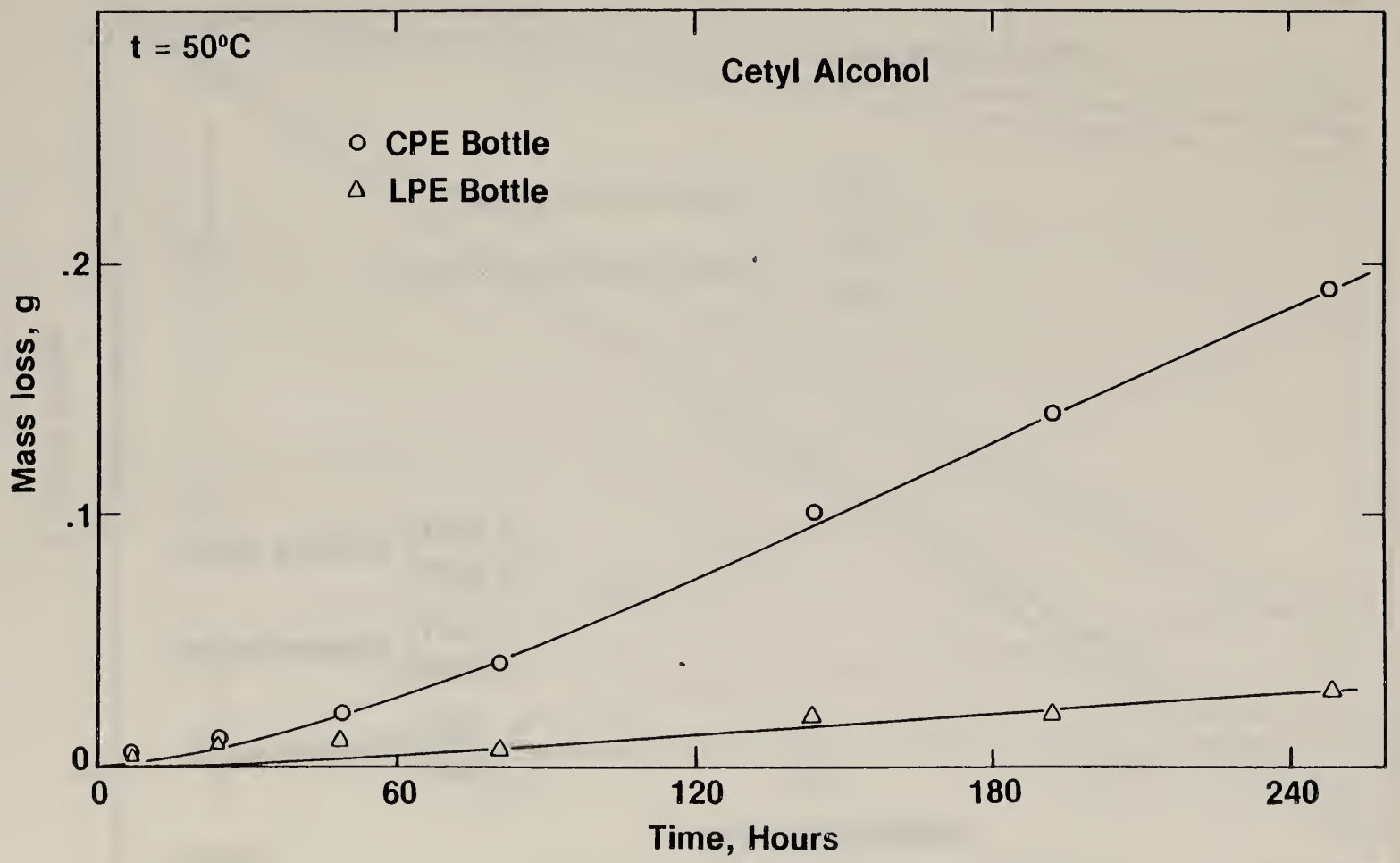
t = 50°C
Cetyl Alcohol
CPE Bottle
LPE Bottle
Mass loss, g
.2
.1
0
0
60
120
180
240
Time, Hours

Fig. 4

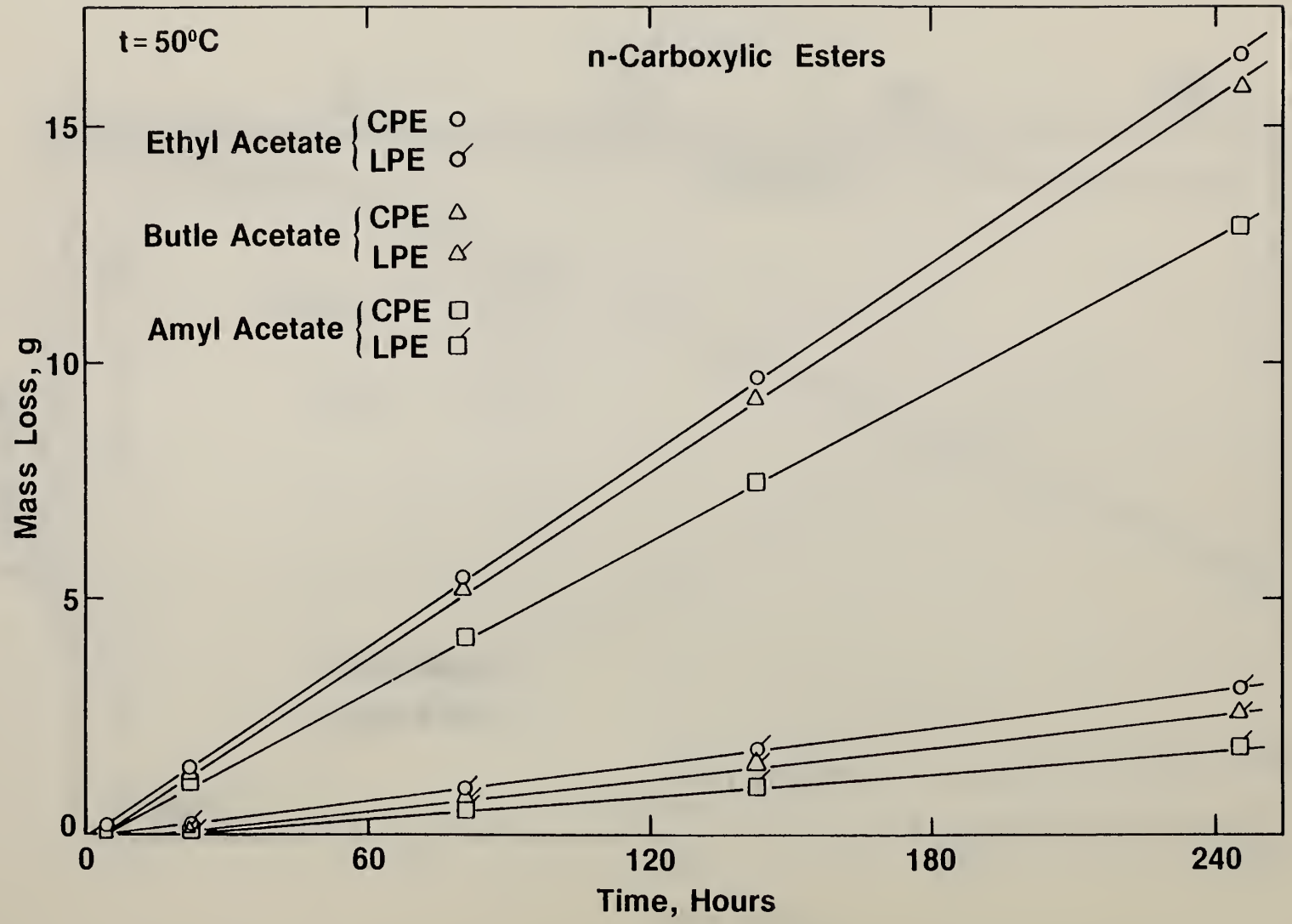
t = 50°C
n-Carboxylic Esters
Ethyl Acetate
CPE
LPE
Butle Acetate
CPE
LPE
Amyl Acetate
CPE
LPE
Mass Loss, g
0
5
10
15
0
60
120
180
240
Time, Hours

Fig. 5

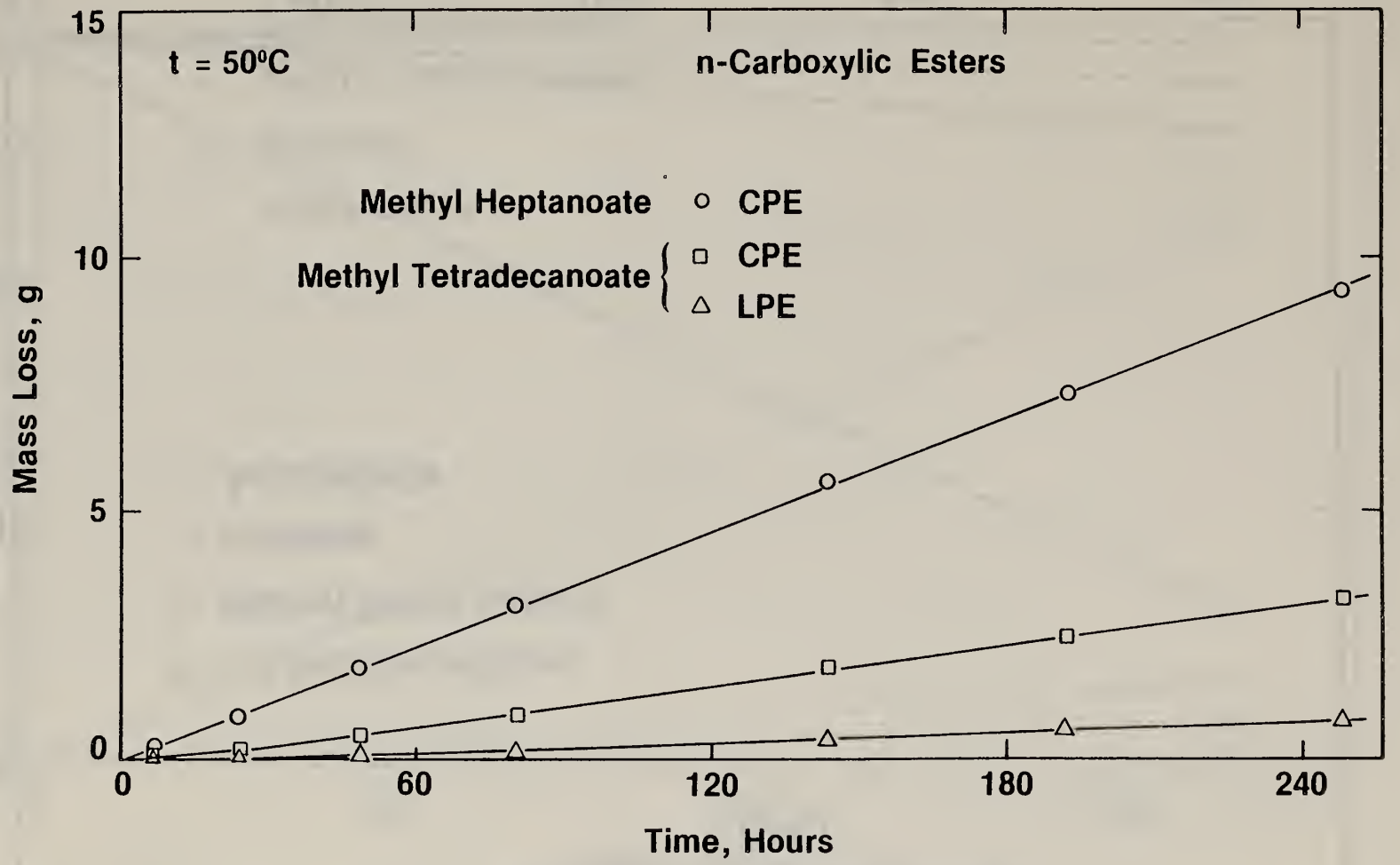
t = 50°C
n-Carboxylic Esters
Methyl Heptanoate
CPE
Methyl Tetradecanoate
CPE
LPE
Mass Loss, g
Time, Hours
0
5
10
15
0
60
120
180
240

Fig. 6

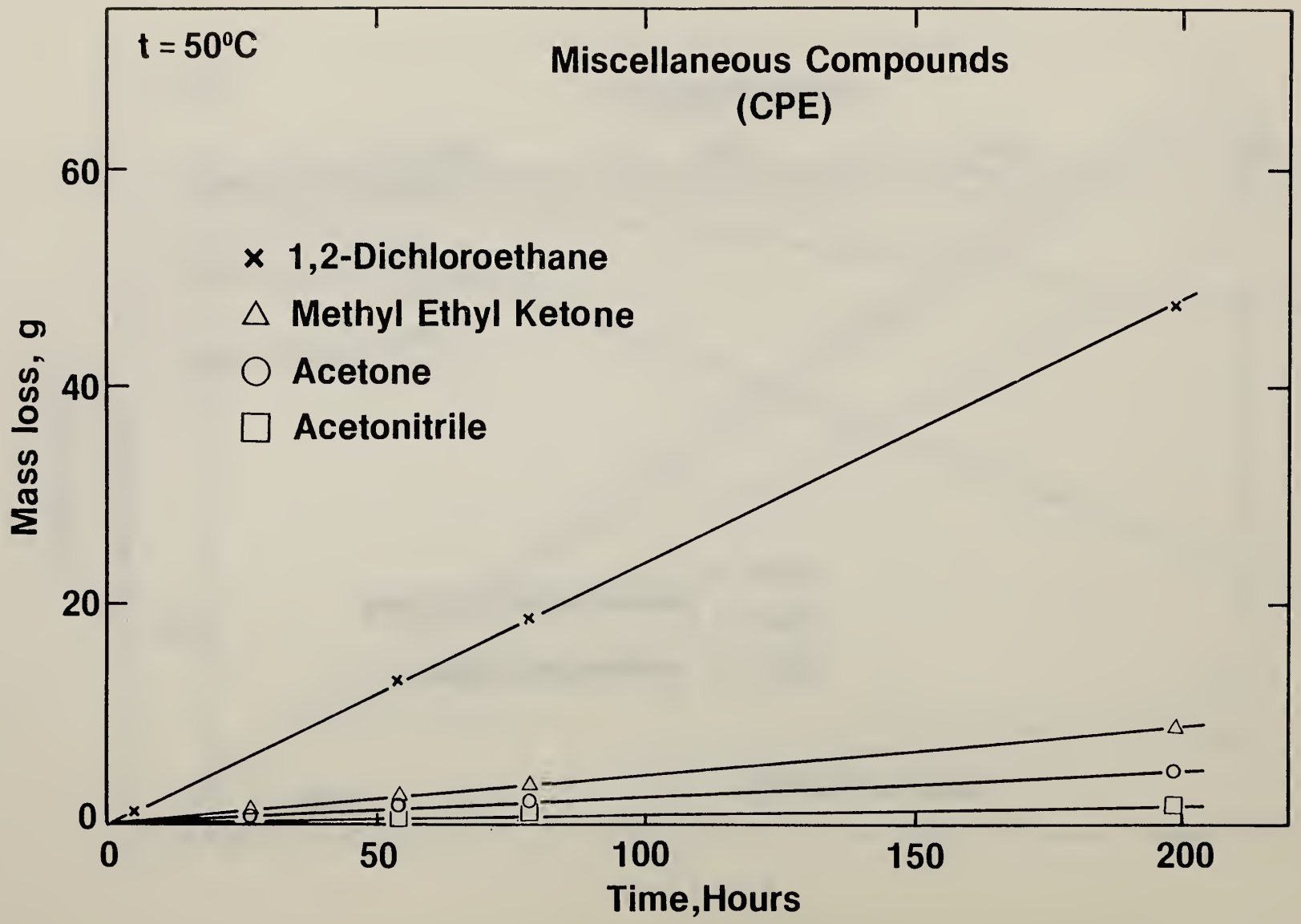
t = 50°C
Miscellaneous Compounds
(CPE)
× 1,2-Dichloroethane
△ Methyl Ethyl Ketone
○ Acetone
□ Acetonitrile
Mass loss, g
0
20
40
60
0
50
100
150
200
Time,Hours

Fig. 7

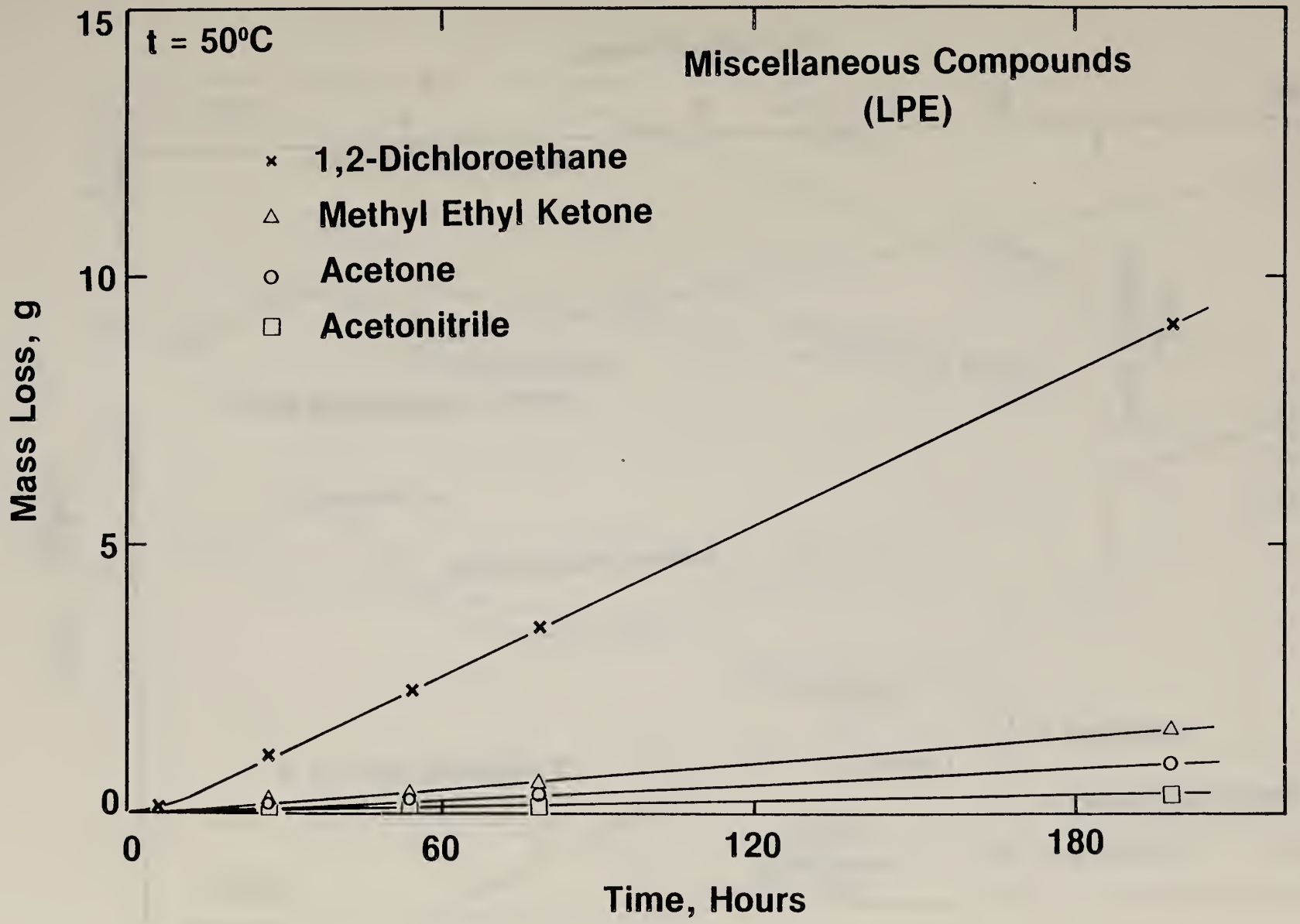
t = 50°C
Miscellaneous Compounds
(LPE)
1,2-Dichloroethane
Methyl Ethyl Ketone
Acetone
Acetonitrile
Mass Loss, g
15
10
5
0
0
60
120
180
Time, Hours

Fig. 8

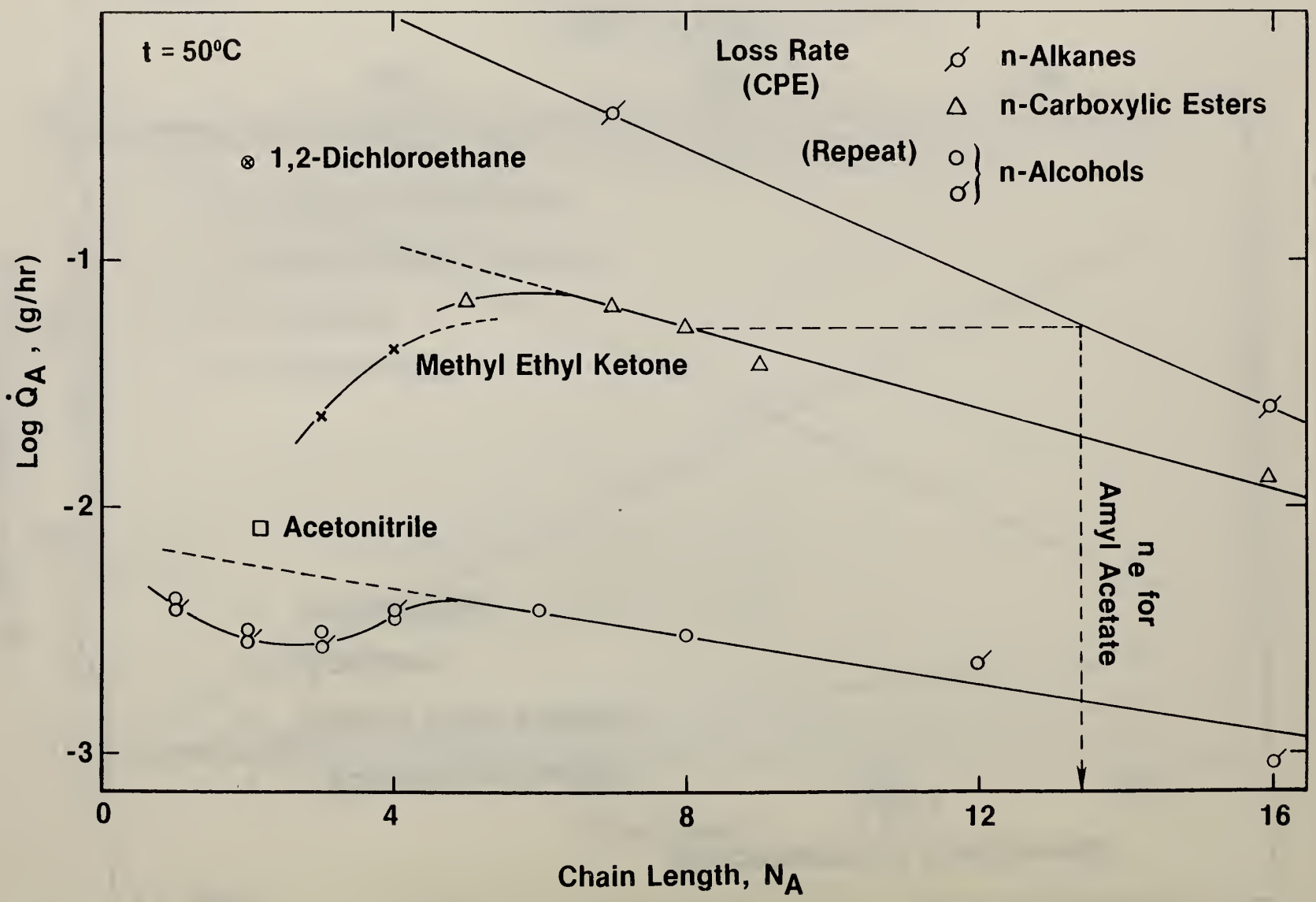
t = 50°C
Loss Rate
(CPE)
n-Alkanes
n-Carboxylic Esters
(Repeat)
n-Alcohols
⊗ 1,2-Dichloroethane
Methyl Ethyl Ketone
□ Acetonitrile
n_e for
Amyl Acetate
Log Q̇_A , (g/hr)
-1
-2
-3
0
4
8
12
16
Chain Length, N_A

Fig. 9

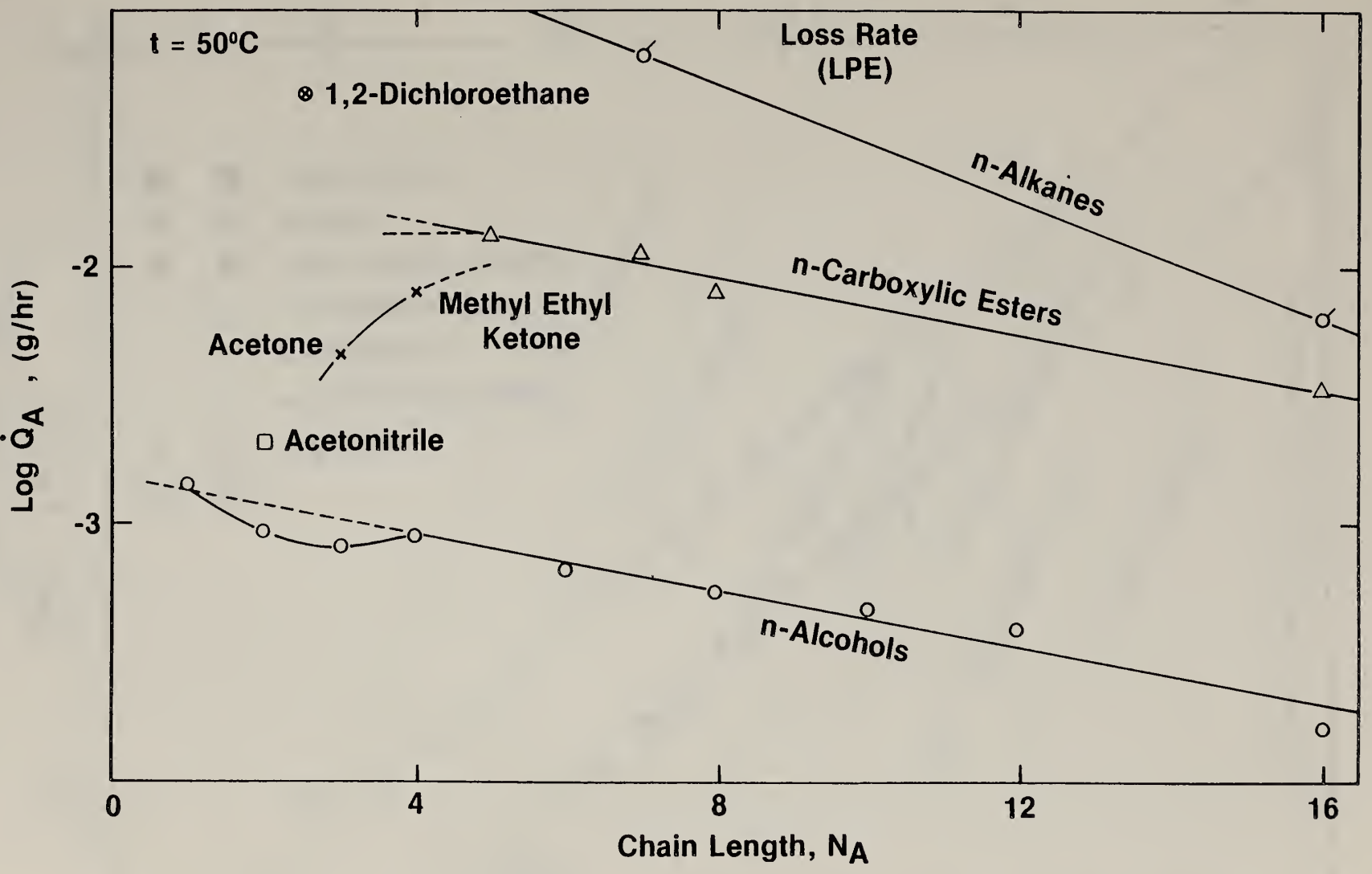
t = 50°C
⊗ 1,2-Dichloroethane
Loss Rate
(LPE)
n-Alkanes
n-Carboxylic Esters
Methyl Ethyl
Ketone
Acetone
□ Acetonitrile
n-Alcohols
Log $\dot{Q}_A$, (g/hr)
-2
-3
0
4
8
12
16
Chain Length, N_A

Fig. 10

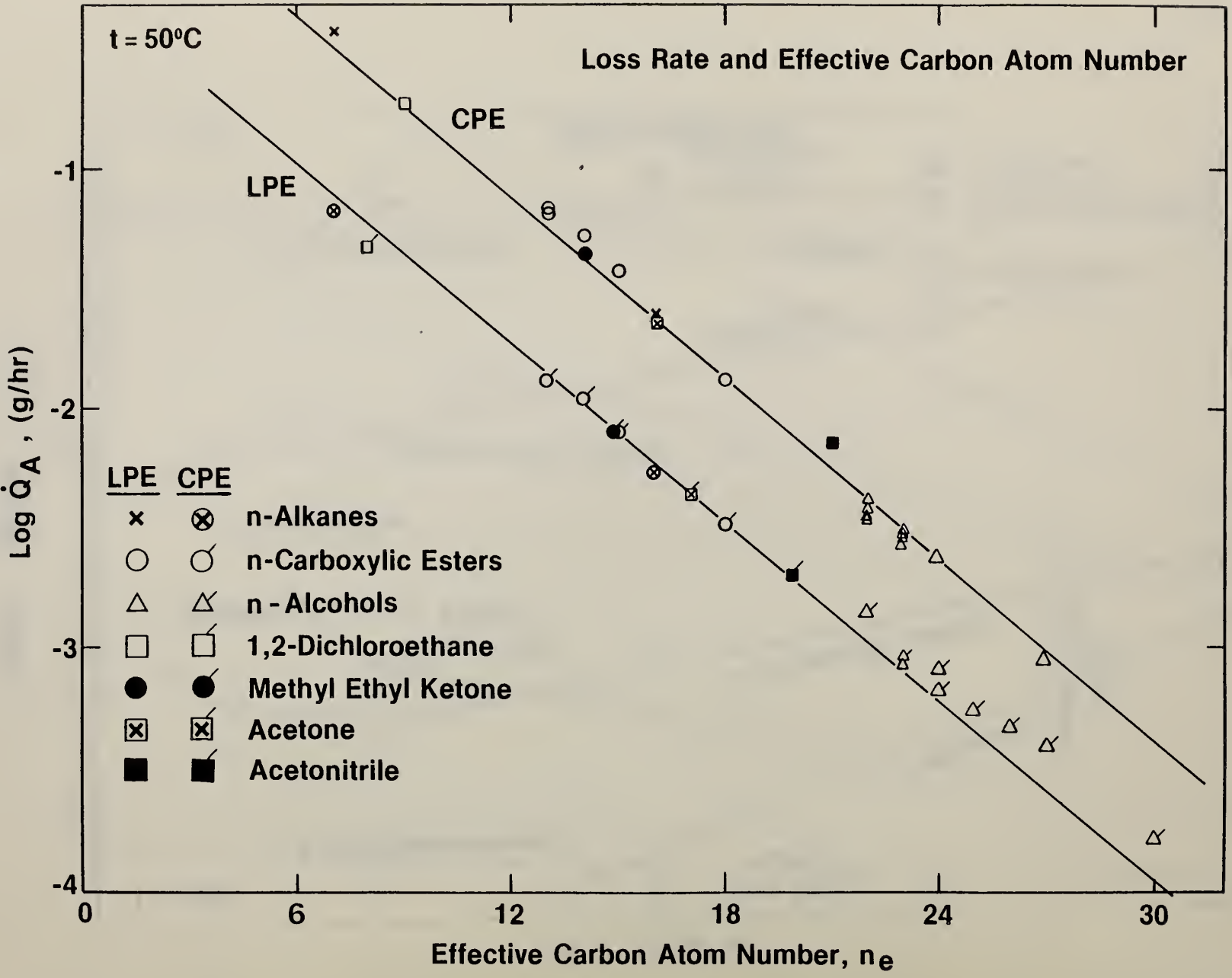
t = 50°C
Loss Rate and Effective Carbon Atom Number
CPE
LPE
Log $\dot{Q}_A$, (g/hr)
-1
-2
-3
-4
LPE CPE
n-Alkanes
n-Carboxylic Esters
n - Alcohols
1,2-Dichloroethane
Methyl Ethyl Ketone
Acetone
Acetonitrile
0
6
12
18
24
30
Effective Carbon Atom Number, n_e

Fig. 11

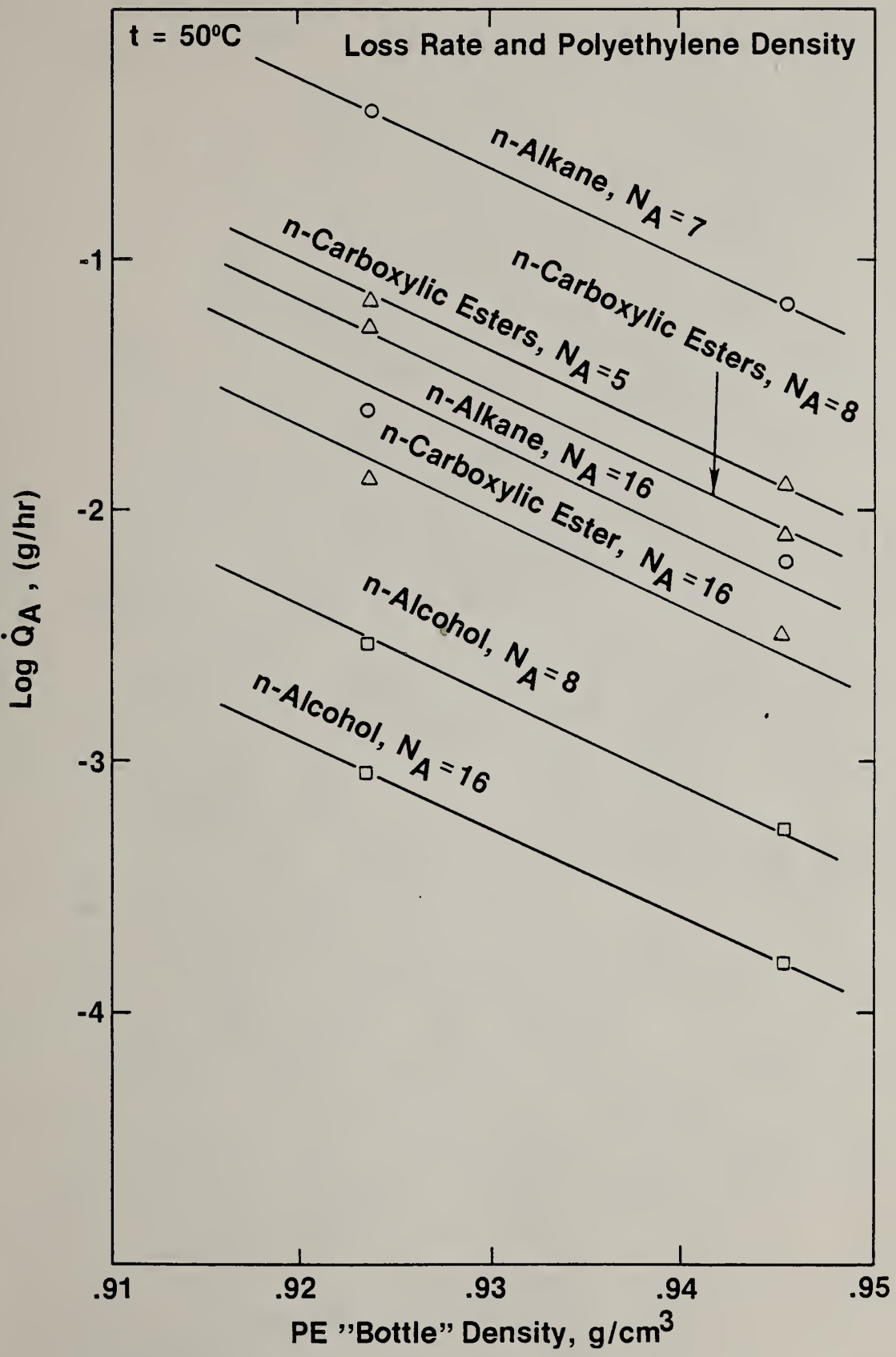
t = 50°C
Loss Rate and Polyethylene Density
n-Alkane, $N_A = 7$
n-Carboxylic Esters, $N_A = 8$
n-Carboxylic Esters, $N_A = 5$
n-Alkane, $N_A = 16$
n-Carboxylic Ester, $N_A = 16$
n-Alcohol, $N_A = 8$
n-Alcohol, $N_A = 16$
Log $\dot{Q}_A$, (g/hr)
-1
-2
-3
-4
.91
.92
.93
.94
.95
PE "Bottle" Density, g/cm^3

Fig. 12